

IN THE UNITED STATE PATENT AND TRADEMARK OFFICE

In re application of :  
 Tatsuhiko SHIBUYA, et al. : Group Art Unit 1755  
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 METHOD BY USING THE SAME :

TRANSLATOR'S DECLARATION

Assistant Commissioner for Patents  
 Washington, D.C. 20231

Sir:

I, Kenji OHDAN, declare:

that I am thoroughly familiar with both the Japanese  
 and English languages;

that the attached document represents a true full  
 English translation of Japanese Patent Kokai 9-208237; and

That I further declare that all statements made herein  
 of my own knowledge are true and that all statements made  
 on information and belief are believed to be true; and  
 further that these statements were made with the knowledge  
 that willful false statements and the like so made are  
 punishable by fine or imprisonment, or both, under Section  
 1001 of Title 18 of the United States Code, and that such  
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 application or any patent issuing thereon.

Signed this *19th* day of *December, 2000*.

*Kenji Ohdan*  
 TRANSLATOR

Translation of Japanese Patent Kokai 9-208237

(54) **【Title of the invention】** Method for the preparation of silica glass

(57) **【Abstract】**

**【Object】** A method is provided, in the method for the preparation of silica glass by the sol-gel method, for preventing crack formation in the low-temperature region during gel-firing process occurring depending on the sol preparation batches.

**【Constitution】** Crack formation in the low-temperature region during the gel-firing process can be effectively prevented by controlling the water content not to exceed 1% by weight in a mixed solution of partial polycondensate of a silicon alkoxide/organic polymer/solvent.

**【The claims】**

**【Claim 1】** A method for the preparation of silica glass characterized in that, in a method for the preparation of silica glass in which a salt and a base are added to a mixed solution of a partial polycondensate of a silicon alkoxide/organic polymer/solvent followed by the addition of water to effect hydrolysis forming a sol and gelation and a dried gel is formed by drying and fired to give glass, the content of water in the mixed solution of a partial polycondensate of a silicon alkoxide/solvent/organic polymer is kept not to exceed 1% by weight.

**【Detailed description of the invention】**

**【0001】**

**【Technological field to which the invention belongs】** The present invention relates to a method for the preparation of silica glass usable for photomasks, jigs for the manufacture of semiconductors, optical members and the like.

**【0002】**

**【Prior art technology】** As one of the methods for the preparation of synthetic quartz glass, proposals are made for the preparation method by the sol-gel method in which a salt and a base are

added to a mixed solution of a partial polycondensate of a silicon alkoxide/organic polymer/solvent followed by the addition of water to effect hydrolysis forming a sol and gelation and a dried gel is formed by drying and fired to give glass (for example, Japanese Patent Kokai). This method has advantages that the step of sol preparation is simple, a large dried gel free from crack can be obtained in the step of drying within a short time, occurrence of foaming and crack formation is less frequent in the step of firing and vitrification of the dried gel and so on. However, when synthetic quartz glass is prepared in a large number by overlaying batches of the sol, a problem took place that occurrence of cracks was found of some batches of the sol in the low temperature region (300 °C or below) in the gel-firing process of the gel obtained thereby decreasing the yield of the glass.

**[0003]**

**[Problems to be solved by the invention]** The present invention provides, in a preparation method by the sol-gel method in which a mixed solution of a partial polycondensate of a silicon alkoxide/organic polymer/solvent is admixed with a salt and a base and then admixed with water to effect hydrolysis forming a sol which is subjected to gelation and drying to give a dried gel and firing to give glass, a method for preventing occurrence of cracks within a low temperature region of the firing process of the gel depending on the sol preparation batches.

**[0004]**

**[Means to solve the problems]** The present invention is a method for the preparation of silica glass characterized in that, in the preparation method of silica glass in which a mixed solution of a partial polycondensate of a silicon alkoxide/organic polymer/solvent is admixed with a salt and a base and then admixed with water to effect hydrolysis forming a sol which is subjected to gelation and drying to give a dried gel and firing to give glass, the content of water in the mixed solution of a partial polycondensate of a silicon alkoxide/solvent/organic polymer is kept not to exceed 1% by weight.

【0005】 The inventors have arrived at a discovery, as a result of the studies on a method for solving the above mentioned problems, that occurrence of cracks in the low temperature region of the gel-firing process is closely correlated with the content of water in the mixed solution of a partial polycondensate of a silicon alkoxide/organic polymer/solvent and that cracks in the low temperature region of the gel-firing process can be efficiently prevented by controlling the content of water in the mixed solution of a partial polycondensate of a silicon alkoxide/organic polymer/solvent not to exceed 1% by weight leading to completion of the present invention.

【0006】

【Practicing mode of the invention】 When the content of water in the mixed solution of a partial polycondensate of a silicon alkoxide/organic polymer/solvent exceeds 1% by weight, cracks are readily formed in the low temperature region of the gel-firing process. For controlling the content of water in the mixed solution of a partial polycondensate/organic polymer/solvent, applicable is one of the methods of using starting materials of low water content, dehydration of each starting material before compounding by distillation, contacting with a suitable dehydrating agent such as zeolites and the like as known, dehydration of the mixed solution of a partial polycondensate/organic polymer/solvent by passing a column filled with a dehydrating material such as zeolites and the like, and so on. Further, increase of the water content in the mixed solution is caused to exceed the amount specified in the present invention also by the water remaining in the reaction vessel, entering of the moisture from the atmosphere in the preparation of the mixed solution of a partial polycondensate/organic polymer/solvent, and so on. Entering of such water to the mixed solution can be prevented to conduct sol preparation with good reproducibility by undertaking a method of strict control of the reaction vessel after use and after cleaning, blowing of dry air, dry nitrogen and the like into the reaction vessel, and so on.

【0007】 As to the partial polycondensate of a silicon alkoxide used in the present invention, the partial polycondensates of silicon tetramethoxide, silicon tetraethoxide, silicon tetrapropoxide and the like can be used but it is preferable to use a partial polycondensate of silicon tetramethoxide in respect of the cost for the starting material and easiness of accomplishing a large glass size.

【0008】 As to the solvent used in the present invention, it is preferable to use a mixed solvent of alcohols such as methanol, ethanol, propanol and the like and solvents of a high boiling point such as dimethylformamide, dimethylacetamide, tetrahydrofurfuryl alcohol and the like in order to increase the size of the glass. As the organic polymer used in the present invention, polyvinyl acetate, polyethyleneglycol and derivatives thereof, hydroxypropyl cellulose and the like can be used.

As the salt used in the present invention, salts of a base such as ammonium hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide, trimethylethylammonium hydroxide (choline) and the like and an acid such as nitric acid, hydrochloric acid and the like can be used. As the basic catalyst used in the present invention, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide and trimethylethylammonium hydroxide (choline) can be used.

【0009】 The sol prepared by using the above described ingredients is poured into a vessel and kept standing to be converted into a gel which is dried to prepare a dried gel. As the method for drying the gel, the applicable method is either of the method utilizing a known gas-permeable film and the method utilizing pin holes. Silica glass can be obtained by vitrifying the thus prepared dried gel by a known method of, for example, heating at a temperature of 1400 to 1500 °C.

【0010】

#### 【Examples】

##### Example 1

A sol was prepared according to the following procedure by using a partial polycondensate of silicon tetramethoxide (water

content 0.05%), methanol (water content 0.02%), dimethylformamide (water content 0.05%), tetrahydrofurfuryl alcohol (water content 0.08%) and polyvinyl acetate (degree of polymerization: 1800). In a Teflon-coated stainless steel vessel after blowing of dry nitrogen thereinto were taken by weighing 100 parts by weight of the partial polycondensate of silicon tetramethoxide, 500 parts by weight of the methanol, 360 parts by weight of the dimethylformamide, 266 parts by weight of the tetrahydrofurfuryl alcohol and 5 parts by weight of the polyvinyl acetate (degree of polymerization: 1800) and they were mixed together for 1 hour. The thus obtained mixed solution (water content 0.2%) of the partial polycondensate of silicon tetramethoxide/methanol/dimethylformamide/tetrahydrofurfuryl alcohol/polyvinyl acetate was admixed with a 1M aqueous solution of choline nitrate to give a choline nitrate concentration of  $5.0 \times 10^{-4}$  mole per 100 g of the partial polycondensate of silicon tetramethoxide and then admixed with a 1M methanol solution of choline to give a choline concentration of  $1.2 \times 10^{-4}$  mole per 100 g of the partial polycondensate of silicon tetramethoxide. After 1 minute of agitation and mixing, 390 parts by weight of water were added. A sol was prepared by further continuing agitation. 4.5 kg of the thus obtained sol were poured into four 480 mm square Teflon-coated stainless steel vessels which were covered with a cover provided with two pin holes of 1 mm diameter. After gelation by standing, the vessels containing the sol were gradually heated from 50 °C to 180 °C to dry the gel. The time for drying was about 10 days. The thus obtained dried gels were heated up to 300 °C in an atmosphere of air to find cracks in none of the gels.

#### 【0011】 Example 2

A mixed solution of the partial polycondensate of silicon tetramethoxide/methanol/dimethylformamide/tetrahydrofurfuryl alcohol/polyvinyl acetate prepared in the same manner as in Example 1 was admixed with pure water under further agitation for 0.5 hour to prepare mixed solutions of which the content of water was 0.4, 0.6 and 1.0 in the solution. Thereafter, by using each of the mixed solutions, a dried gel (each in 4

plates) was prepared in the same manner as in Example 1 and the thus prepared dried gels were heated up to 300 °C in an atmosphere of air to check occurrence of cracks. No cracks were found in each case.

**[0012] Comparative Example 1**

A mixed solution of the partial polycondensate of silicon tetramethoxide/methanol/dimethylformamide/tetrahydrofurfuryl alcohol/polyvinyl acetate prepared in the same manner as in Example 1 was admixed with pure water with further agitation for 0.5 hour to prepare mixed solutions of which the content of water was 1.5, 2.0 and 2.5% in the solution. Thereafter, by using each of the mixed solutions, a dried gel (each in 4 plates) was prepared in the same manner as in Example 1 and the thus prepared dried gels were heated up to 300 °C in an atmosphere of air to check occurrence of cracks. Occurrence of cracks was found in two of the four gels when the water content in the mixed solution of the partial polycondensate of silicon tetramethoxide/methanol/dimethylformamide/tetrahydrofurfuryl alcohol/polyvinyl acetate was 1.5% while in four of the four gels with 2.0% and 2.5%.

**[0013]**

**[Advantages of the invention]** According to the present invention, large-size quartz glass free from cracks by the sol-gel method can be prepared with stability and a large contribution can be made to price reduction of silica glass.